#### DELTA-DOPED CCDS FOR ENHANCED UV PERFORMANCE

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#### Abstract

Thin, backside-illuminated CCDs are modified by growing a delta-doped silicon layer on the back surface using molecular beam epitaxy. Delta-doped CCDS exhibit stable and uniform 100% internal quantum efficiency. The process consists of growth of an epitaxial silicon layer on a fully-processed commercial CCD die in which 30% of a monolayer of boron atoms are incorporated into the lattice nominally in a single atomic layer. Long term stability was tested and showed no degradation of the device quantum efficiency over sixteen months. Reduction of the reflectivity of the Si surface by deposition of HfO<sub>2</sub> on the CCD back surface further increased the QE, with measured QE over 80% in some regions of the spectrum. We will discuss these results as well as the delta-doped CCD concept and process.

#### 1. Ultraviolet\_detection\_with\_silicon CCDs

The highest UV quantum efficiency (QE) in silicon CCDs is obtained by backside-illumination of thinned devices. However, positive charge in the Si/SiO<sub>2</sub> interface creates a potential well which traps photoelectrons at the CCD back surface. The detection of ultraviolet light in Si CCDS has been a long-standing challenge, due to the short absorption length of UV photons in silicon and the existence of this potential well. To put this problem in perspective, the absorption depth of UV photons in silicon drops to a minimum of 40 Å at about 270 nm, and is less than 100 Å over the range of wavelengths from 90 nm to 360 nm. In comparison, the backside potential well typically extends -0.5 µm into the silicon lattice, preventing detection of photoelectrons produced within that region. Improvement of the UV quantum efficiency is accomplished by placing a high concentration of negative charge must be placed as close as possible to the back surface in order to obtain the maximum possible quantum efficiency.

The first solutions to this problem involved treating the back surface of the CCD by surface charging (i.e., UV-flood, biased flash-gate), resulting in reasonable or high UV quantum efficiency. However, these treatments suffer variously from problems of yield, response stability, hysteresis, and long-term reliability. Stability of the quantum efficiency has great impact on astronomical measurements, particularly in space-based applications where renewal of the back surface treatment (e.g., by exposing the device to intense UV light) is not an attractive option.

Elimination of the potential well by the introduction of a thin layer of p+ doped silicon results in stable, high quantum efficiency, provided that the dopant concentration is sufficiently high and the p<sup>+</sup> layer is sufficiently thin. The first attempts at this solution used ion implantation of the CCD back surface.<sup>3</sup> However, the quantum efficiency obtained by ion implantation does not approach the theoretical limit. While the MBE-modification of thin CCDS is conceptually similar to ion implantation, there are fundamental differences in the techniques of incorporation of negative charge in the lattice, post charge-incorporation processes, and resulting performance of these processes. Because ion implantation damages the lattice and leaves many of the dopant atoms in inactive sites in the lattice, post-implantation

annealing is usually required. After the MBE process, the CCD does not require annealing for incorporation of the dopant atoms or removal of damage to the lattice.

Using MBE, delta-doped CCDS with highly stable and uniform quantum efficiency in the visible and near UV have been fabricated.<sup>4</sup> The quantum efficiency of these devices is limited by the reflection of the photons from the back surface and can be enhanced by deposition of antireflection (AR) coatings. In this paper, we describe the growth of delta-doped silicon on commercial CCDs using MBE, and the resulting enhancement of the UV quantum efficiency. Deposition of antireflection coatings on delta-doped CCDS is also discussed. The characteristics of the modified CCDs, such as the uniformity and stability of the quantum efficiency, are described.

## 2, MBE modification of CCDs

MBE modification of CCDS has the dual advantages of high stability inherent in the p⁺doped layer and high quantum efficiency due to the unique dopant profiles attainable in MBE-grown silicon. Calculations of the surface potential in silicon show that the dopants must be located within a few nanometers of the surface to obtain the maximum possible quantum efficiency.⁴The high dopant concentrations necessary for the removal of the backside potential (at least 10¹⁴ B/cm²) and the exacting requirements for its positioning (≈ 1 nm from the interface) can be achieved by MBE, but are beyond the limits of ion implantation.

Epitaxial silicon is grown on the carefully prepared back surface of thinned, fully-processed devices (Fig. 1). The MBE-grown epilayer, with a thickness of only ~ 6 atomic layers, contains 30% of a monolayer of p-type dopant (boron) atoms. The boron atoms are incorporated into the lattice approximately 5 Å below the Si-SiO<sub>2</sub> interface, providing the necessary negative charge for band bending at this interface so that the photoelectrons produced are not trapped near the interface and are instead captured in the front potential well. Recent advances in low temperature substrate cleaning techniques<sup>5,6</sup> have enabled MBE growth on thin CCDs. During the pre-MBE cleaning and epitaxial growth, the CCD temperature is never raised above 450°C. Exceeding this temperature could cause the diffusion of metal contacts into the silicon and damage the CCD. For example, temperatures exceeding 500°C will damage Reticon CCDS due to spiking of the Al contacts into the underlying silicon. Also, at this temperature, boron does not diffuse and forms an extremely thin layer of negative charge 5 Å below the Si/SiO<sub>2</sub> interface.

The details of the delta-doping process are described in previous papers. <sup>4</sup>, 7-9 The major steps of the process are outlined below. Fully-processed Reticon CCD die, complete with aluminum contacts are thinned at Reticon, using gold as a thinning mask. <sup>10</sup> This process leaves the CCD with a thick frame, from which the gold mask has to be removed before MBE. After the chemical removal of the gold, the CCD was cleaned by a series of solvents to remove residual photoresist, wax, and contamination from handling and gold-removal process. The CCD was then exposed to UV-generated ozone in a nitrogen glove box, which removes residual hydrocarbons but leaves the surface oxidized, Also under nitrogen, this oxide is removed by dispensing 10% HF in ethanol solution on the CCD while the device is spinning. The CCD is transferred to the MBE vacuum chamber and slowly heated at 100°C, 200°C and 300°C for five minute intervals at each temperature. The CCD is finally heated to 450°C and stays at this temperature for about one minute before the growth. With MBE the following structure is grown on the backside of the device:10 Å of boron-doped Si (4 x 10<sup>20</sup> boron/cm<sup>3</sup>), a delta layer consisting of 2 x 10<sup>14</sup> boron/cm<sup>2</sup>, and a protective layer consisting of 15 Å of undoped Si. The CCD is transferred out of the chamber and is steam oxidized and in the process of steam oxidization part of the 15 Å Si cap layer is consumed. Figure 1 schematically shows the delta-doped layer structure grown on the backside of a thinned CCD. Packaging and testing of delta-doped C-CDS are performed at Reticon. The results presented in this paper are from MBE-modified Reticon 512x 512 CCDs.

Transmission electron microscope (TEM) studies of this technique have shown that the additional delta layer grown by MBE is indistinguishable from the original lattice and that the density of defects at the substrate-epilayer interface or the delta layer is very small and below the TEM detection limit. Note that, unlike ion implantation, no annealing is performed on the lattice after the MBE process to incorporate the boron in the lattice or remove darnage. Deposition of Si is performed by electron beam evaporation, which produces potentially damaging x rays. However, the total x-ray dose received during the MBE modification of the CCD is about 6 krad, which is significantly below the damage threshold of the device. Measurements of the dark current and CTE have shown that the delta-doped CCD exhibits the same characteristics as a typical Reticon 5 12x5 12 CCD of this grade and that there is no evidence of damage to the CCD. If necessary, electron beam evaporation can be replaced by thermal evaporation of silicon to avoid exposure of the CCDs to x rays.

#### 3. Quantum efficiency of delta-doped CCDs

Figure 2 shows the quantum efficiency of bare and antireflection-coated delta-doped CCDs measured at EG&G Reticon. Also shown in the figure, in solid line, is the silicon transmittance which represents the reflection-limited quantum efficiency. The uncoated delta-doped CCD responds at the theoretical limit in the measured region (250-700 nm) at 100% internal quantum efficiency. Note that because the primary limitation to the internal quantum efficiency is the band structure near the back surface relative to absorption length of photons in *silicon*, the most stringent test of the CCD quantum efficiency is the QE at 270 nm, where the minimum absorption length occurs implying that at shorter wavelengths the response will follow approximately the transmittance curve, modified by the effects of oxide absorption and quantum yield of silicon. Also, note that because the backside potential is almost completely removed, (well width ≤5 Å) quantum efficiency hysteresis is also eliminated. Also

From the data in figure 2, it is apparent that reflection from the back surface limits the quantum efficiency of delta-doped CCDs. Reducing the loss due to reflection produces dramatic improvement in the measured quantum efficiency. Direct deposition of antireflection layers on delta-doped CCDS was demonstrated by depositing two HfO<sub>2</sub> films to enhance the quantum efficiency in two different regions of the spectrum. A 400 Å HfO<sub>2</sub> film was deposited to enhance the response in the 300-400 nm range, and a 250 Å HfO<sub>2</sub> film was deposited to enhance the quantum efficiency near 270 nm. The HfO<sub>2</sub> layers were deposited in the University of Arizona's Steward Observatory CCD laboratory, using resistive heating to evaporate the HfO<sub>2</sub>. Details of the experiment can be found in otherpublications.7111 The response of the AR-coated delta-doped CCD is shown in Fig 2 along with the quantum efficiency of the uncoated areas on the same CCD. The response of the AR-coated regions shows the expected enhancement in the quantum efficiency.

# 4. Stability and uniformity of delta-doped CCDs

The uniformity of a delta-doped CCD is demonstrated in Fig. 3, which shows a typical plot of the response of pixels in a column taken at 350 nm. The small variations of the response (3:3%) shown in the figure are typical of512 x 512 Reticon CCDS. The flat field response of delta-doped CCDS show high uniformity with only a few blemishes, well within the normal range for the grade of CCDS used in our experiments. The uniformity of the CCD response was also tested by measuring the quantum efficiency in different regions of the same device. The measurements on three 50x50 pixel areas were performed at the same time under identical conditions and the quantum efficiencies in the three regions were identical (Fig. 4). The inset in the figure shows the approximate position of the three test areas in the array. The pixel-to-pixel variation of the response within each test region is about 1 -2%.

Delta-doped CCDS have been characterized in different measurement setups and have shown in each case 100% internal quantum efficiency. During the intervals between QE measurements and deposition

"of antireflection coatings, the devices have been stored in air in an antistatic box with no further protection. Sixteen months after the MBE process, and after exposure to three different vacuum and camera systems, the quantum efficiency of one of these devices was again measured. Within the accuracy of the measurement, the device has shown no change from the ideal UV response, despite repeated temperature cycling and exposure to different environments.

#### 5. Summary

Quantum efficiency of backside-illuminated CCDS is enhanced to the reflection limit by using MBE to incorporate 30% of a monolayer of boron atoms 5 Å below the backside silicon crystal surface. The response of delta-doped CCDs is highly uniform and these devices have exhibited long-term stability. The total quantum efficiency of the CCD can be enhanced by antireflection coatings, as has been demonstrated by depositing HfO<sub>2</sub> on a delta-doped CCD optimized for the wavelength range of 250-400 nm.

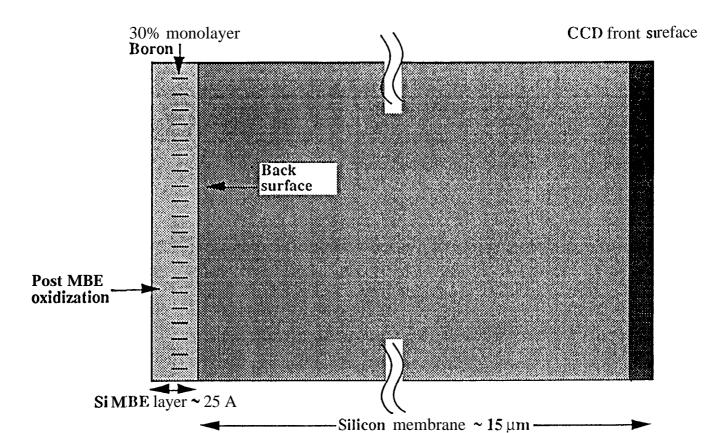
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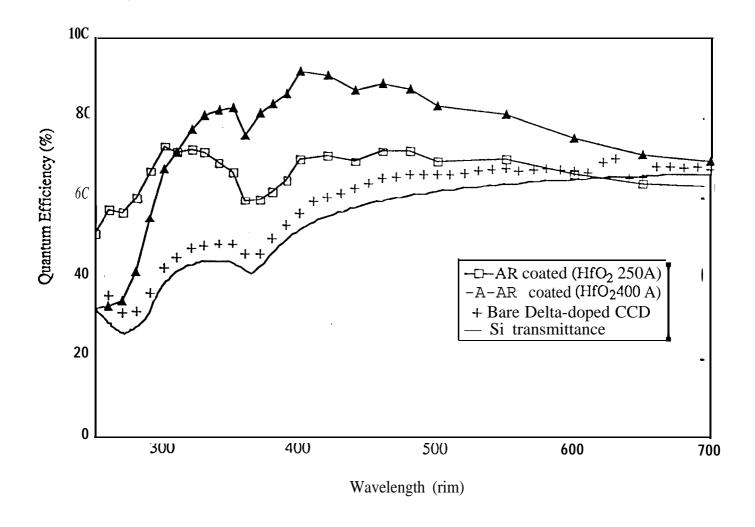
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**Figure 1** Schematic of the layer structure of a delta-doped CCD, shown in cross section. The layers added by MBE are a total of 2.5 nm in thickness, and contain  $-2.5 \times 10^{14}$  p-type dopant (boron) atoms.



**Figure 2.** Quantum efficiency of a delta-doped CCD. Comparison with the reflection-limited quantum efficiency (transmittance of silicon) shows that the delta-doped CCDs exhibit 100% internal quantum efficiency. Deposition of 250 Å and 400 Å of HfO<sub>2</sub> maximize the total quantum efficiency of the device in different parts of the spectrum.

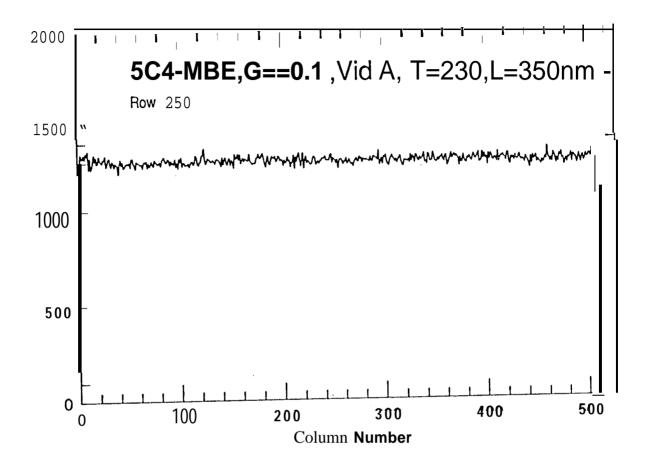
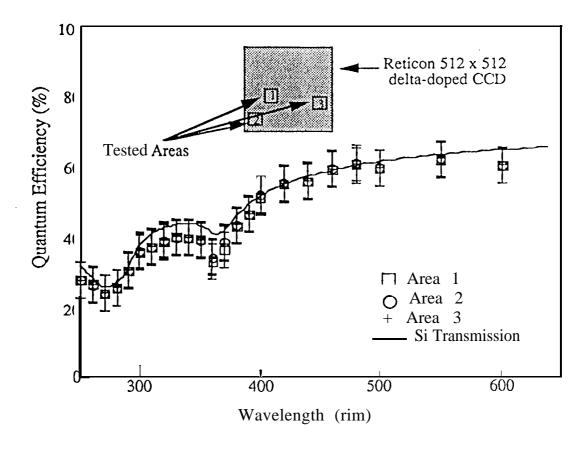


Figure 3. A typical line plot of a delta-doped CCD at 350 nm.



**Figure 4.** Spectral uniformity of a delta-doped CCD measured on three 50x50 pixel areas of the device. The response in these three regions is identical,